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Low-energy electron scattering by C_3H_6 isomers

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We report cross sections for the elastic scattering of electrons by the C_3H_6 isomers propene and cyclopropane from 5 to 40 eV. These results were calculated within the static-exchange approximation, using the Schwinger multichannel method as implemented on the Touchstone DELTA distributed-memory parallel computer. The integral elastic cross sections so obtained support recent observations of a substantial isomer effect in the total scattering cross section. Partial-wave analysis indicates the presence of an unusual A_2' shape resonance in cyclopropane.

I. INTRODUCTION

Collisions between low-energy electrons and small hydrocarbons are important in several contexts, notably in low-temperature plasma-polymerization reactors[1] and near the edges of fusion plasmas contained in graphite-lined vessels.[2] Electron collision cross sections for hydrocarbons larger than C_2H_6 have, however, as yet been little studied. To cite a few examples, momentum-transfer cross sections below 1 eV have been determined in some cases,[3] and excitation functions obtained by the trapped-electron technique have been reported for a few species, including cyclopropane[4] and propene.[5] For most of these larger hydrocarbons, however, the total electron scattering cross section is the best characterized quantity. Total cross sections for propane and *n*-butane were measured by Brüche,[6] and have since been remeasured by Floeder and co-workers,[7] who also gave results for cyclopropane, propene, isobutane, and 1-butene. Nishimura and Tawara[8] have also reported total cross sections for propane, cyclopropane, and propene, and Sueoka[9] has measured the total cross section for benzene. On the theoretical side, we have recently published[10] differential and integral elastic cross sections for propane (and other hydrocarbons), obtained within the static-exchange approximation. In this work we apply the same approximation to the C_3H_6 isomers.

Floeder and co-workers[7] observed small differences (10% or less) in the magnitude of the cyclopropane and propene cross sections around the broad maximum at 10 eV, while Nishimura and Tawara[8] saw a larger effect, with differences of up to 20%. One of the goals of the present work is to determine the magnitude of the isomer effect in the elastic cross section, which is the principal component of the total cross section at these energies. We also wish to look for similarities and differences in the differential and momentum-transfer cross sections, which may help in understanding the underlying scattering dynamics.

Accurate calculations of electron collision cross sections for such hydrocarbons can be quite "compute-intensive," and we have accordingly implemented[11] the SMC procedure on distributed-memory parallel computers, which provide a more cost-effective source of cycles than conventional supercomputers. Previous applications[10–12] have demonstrated the value of this approach and have furthermore confirmed the utility of static-exchange calculations in providing semiquantitative elastic cross sections for low-energy scattering by larger polyatomics.[10,11] The present results were obtained using our parallel SMC program on the Intel Touchstone DELTA, a 520-node machine based on the i860 processor, which was recently delivered to the Concurrent Supercomputing Consortium.[13]

In Sec. II we summarize the SMC method and give details of the calculations. Section III presents the results, which are discussed in Sec. IV.

II. THEORETICAL AND COMPUTATIONAL

These calculations used the Schwinger multichannel (SMC) method, which has been described previously.[14] Briefly, a variationally stable approximation

$$f(\mathbf{k}_m,\mathbf{k}_n) = -1/2\pi \times \frac{\langle \Psi_m^{(-)}(\mathbf{k}_m)|V|S_n(\mathbf{k}_n)\rangle\langle S_m(\mathbf{k}_m)|V|\Psi_n^{(+)}(\mathbf{k}_n)\rangle}{\langle \Psi_m^{(-)}(\mathbf{k}_m)|A^{(+)}|\Psi_n^{(+)}(\mathbf{k}_n)\rangle} \tag{1}$$

to the scattering amplitude $f(\mathbf{k}_m,\mathbf{k}_n)$ is employed, where

$$A^{(+)} = \left(\frac{1}{N+1} - P\right)\hat{H} + VP - VG_P^{(+)}V, \tag{2}$$

with $\hat{H} = E - H$, where H is the full Hamiltonian. P is a projector onto open channels, V the interaction potential between the scattering electron and the molecular target, and $G_P^{(+)}$ the projected free-particle Green's function. The functions $S_{m,n}$ in Eq. (1) are the interaction-free solutions, i.e.,

$$S_m(\mathbf{k}_m) = \Phi_m(\mathbf{r}_1,\ldots,\mathbf{r}_N)\exp(i\mathbf{k}_m\cdot\mathbf{r}_{N+1}), \tag{3}$$

Φ_m being a state of the target. Using an expansion of $\Psi^{(\pm)}$ in spin-adapted $(N+1)$-electron Slater determinants χ_i of Cartesian Gaussian molecular orbitals and imposing variational stability leads to working equations of the form

[a] Contribution No. 8532.

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$$\underline{A}\mathbf{x} = \mathbf{b}, \tag{4}$$

with $A_{ij} = \langle \chi_i | A^{(+)} | \chi_j \rangle$ and $b_i = \langle \chi_i | V | S_0(\mathbf{k}) \rangle$, where S_0 is the interaction-free wave function in the elastic channel; from the vectors $\mathbf{x}$ and $\mathbf{b}$, the elastic scattering cross section may be determined. All matrix elements needed to construct $\underline{A}$ and $\mathbf{b}$ are obtained analytically except those of $VG_P^{(+)}V$, which are obtained by numerical quadrature in the momentum variable of $G_P^{(+)}$.[15]

Two Cartesian Gaussian basis sets were used in these calculations, both extensions of Dunning's[16] $4s3p$ (carbon) and $3s$ (hydrogen) contracted basis sets. The first basis contained in addition one s, one p, and one d function on each carbon (exponents 0.0473, 0.0365, and 0.2, respectively), for a total of 87 contracted functions. Convergence with respect to basis set was tested by repeating the calculations in a larger basis, consisting of the same Dunning basis supplemented by two d functions on each carbon (exponents 0.8 and 0.2) and one p (exponent 0.1) on each hydrogen, totaling 111 contracted functions. Differences between the cross sections obtained in the two basis sets were minor above 5 eV; the results presented below were obtained in the larger basis. Errors arising from the basis set and the numerical quadrature of $VG_P^{(+)}V$ are estimated to be no more than 5–10 % over the range of energies reported, and to be comparable to or less than errors arising from the fixed-nuclei static-exchange approximation itself.

Propene has a small permanent electric dipole moment (experimental value[17] 0.366 D; 0.405 D in the present calculation). As a result, the fixed-nuclei integral cross section formally diverges, due to a logarithmic divergence of the differential cross section in the forward direction. Procedures have been devised for treating dipolar molecules,[18] most based on the idea that the lower partial waves can be obtained accurately from a fixed-nuclei calculation, while the higher partial waves, which "see" only the long-range dipole potential, can be generated with very little error via a simple (e.g., Born) approximation. Thus we might drop the infinite contribution of the higher partial waves to the fixed-nuclei cross section and replace it with the corresponding Born value[18] for a rotating dipole. However, if the dipole moment is sufficiently small, it is reasonable to expect that simply truncating the fixed-nuclei integral cross section at some finite angular momentum l will also yield a good approximation to the rotationally summed elastic cross section, and that the differential cross section so generated will be meaningful at all but the smallest angles. How small the dipole moment must be for this simple approach to be valid depends on the rotational constants of the molecule and on the scattering energies of interest. For example, using parameters appropriate for scattering from propene at 5 eV and above, the integral cross section for a rotating dipole in the Born approximation is on the order of 2×10^{-16} cm^2 at most. As will be seen below, this is a small fraction of the actual propene cross section. Similarly, the differential cross section in the same approximation is much less than 10^{-16} cm^2/sr above 10°, although it becomes extremely large at 0°. Little error is therefore introduced by neglecting the Born correction.

In the present calculation, use of a finite basis and of a finite number of $\hat{k}$ directions in performing numerical quadratures introduces an effective cutoff in l, and no explicit cutoff is required to avoid divergences. Since the individual partial-wave contributions are already quite small by the time this effective cutoff is reached, its precise value is not important, except to determine at how small an angle the differential cross section is meaningful. We estimate that the differential cross section is essentially unaffected by absence of the high-l dipole-scattering terms down to at least 10° for all of the energies considered.

Performance of the SMC method on the Touchstone DELTA is still far from optimal. In part this reflects the newness of the system; we have not done extensive optimization, and the *i*860 compilers do not yet generate efficient code in many cases. Performance in the present application also reflects the nature of the SMC program. In a general scattering calculation, where many channels are open, most of the floating-point work will go into the data manipulation required in constructing the $(N+1)$-electron matrix elements; this step involves only linear algebra and can be made highly efficient. For single- or few-channel studies in large molecules, however, the most computationally intensive step is the analytic evaluation of two-electron integrals $\langle \alpha(\mathbf{r}_1)\beta(\mathbf{r}_1)(1/r_{12})\gamma(\mathbf{r}_2)\exp(i\mathbf{k}\cdot\mathbf{r}_2)\rangle$, where α, β, and γ are Cartesian Gaussians. The operations needed in the integral-evaluation routines—recursions, intrinsic-function calls, and branching logic—execute slowly when compared to the vector multiplications and additions which predominate in linear algebra. Nonetheless, present SMC performance, with an overall sustained rate of about 2 MFlop per processor, compares very favorably to that of the sequential SMC code on CRAY-type machines. The results presented below were obtained with independent calculations executing simultaneously on 256-processor partitions of the DELTA.

III. RESULTS

Figure 1 shows the calculated integral elastic cross sections for cyclopropane and propene, along with total cross section measurements of Floeder and co-workers[7] and of Nishimura and Tawara.[8] A broad maximum, centered at approximately 10 eV in the experimental total cross sections and 12 eV in the theoretical elastic cross sections, is observed for both molecules. A similar maximum is seen in scattering by many other hydrocarbons,[6–9] although the peak usually falls near 8 eV. Both the experimental and the theoretical cross sections show an isomer effect at low energies, with the propene cross section larger than that of cyclopropane, particularly near 10 eV. At higher energies, the calculated elastic cross sections converge, as do the total cross sections of Ref. 8. A feature of the computed propene cross section not seen experimentally is the rise at the low-energy side of the figure. This results from the tail of the low-energy π^* shape resonance, which, like the broad maximum, is placed at too high an energy (4 eV) in the static-exchange approximation. Experimentally, this resonance falls at 2 eV,[19] and it does not greatly affect the scattering at 5 eV and above.

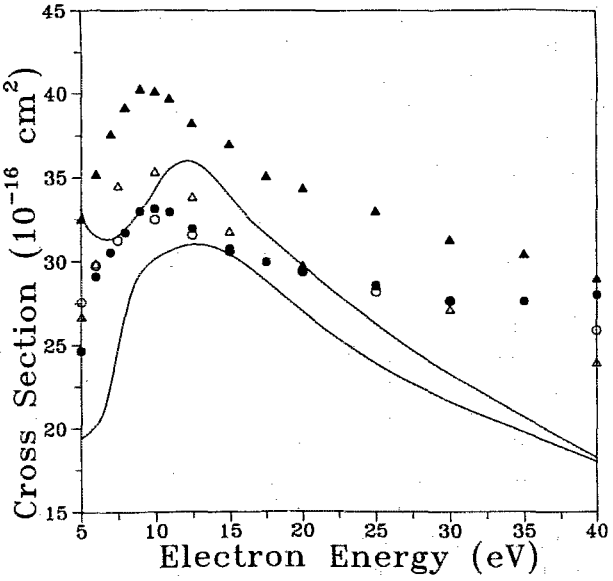

FIG. 1. Calculated integral elastic cross sections for propene (upper curve) and cyclopropane (lower curve). For purposes of comparison, total scattering cross sections of Refs. 7 (open symbols) and 8 (filled symbols) are shown. Triangles are propene data and circles cyclopropane.

Figure 2 shows the decomposition of the cross sections into symmetry components which are either even or odd with respect to the plane defined by the three carbon nuclei. For propene, the even component corresponds to the A' irreducible representation of the C_s group and the odd component to A''; for cyclopropane, even and odd include the representations (A_1',A_2',E') and (A_1'',A_2'',E'') of D_{3h}, respectively. The isomeric difference in the magnitude of the integral cross sections is seen to reflect a larger even component in propene, the odd contributions being roughly equal. Also, the even component in cyclopropane exhibits two maxima, a narrow one at approximately 8.5 eV and a broad one near 13 eV. On further analysis, the narrow peak is found to arise from the $(l_{out},m_{out}) = (3, \pm 3)$ portion of the scattering amplitude (in a coordinate system with the z axis perpendicular to the CCC plane). This component and some of the other large partial-wave contributions are shown in Fig. 3. The broad peak is seen to contain a mixture of waves, the single largest contributor being $(l_{out},m_{out}) = (3, \pm 1)$. A similar breakdown for propene (Fig. 4) shows that $l = 3$, $m = \pm 3$ makes a large contribution in this case also; however, there is no such sharp structure as was seen for cyclopropane.

In contrast to the elastic cross sections, the calculated momentum-transfer cross sections (Fig. 5) show quite a small isomer effect, with a significant difference seen only on the low-energy side of the maximum. The peak in the momentum-transfer cross section is also seen to fall at a slightly lower energy than the elastic scattering peak.

In Figs. 6 and 7 we present differential cross sections at selected energies for both isomers. The propene differential cross section is relatively unstructured, while at low energy there is significant oscillation in the cyclopropane cross section. Otherwise, the principal difference between the two molecules is in the strength of the forward scattering. Over most of the energy range, forward scattering by propene is considerably stronger, with the near-forward angles accounting for most of the difference seen in the integral elastic cross sections. At the highest energies, where the integral cross sections are almost equal, this difference in forward scattering begins to decrease, and the differential cross sections for the two molecules become very similar.

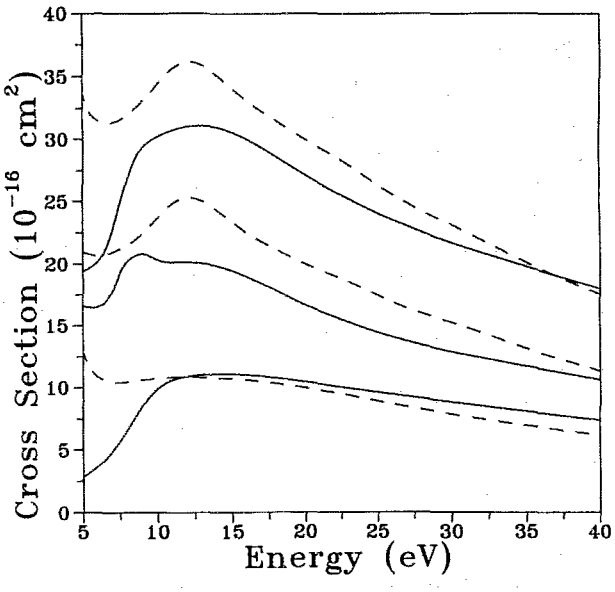

FIG. 2. Breakdown of the integral elastic cross section (top curves) into components even (middle curves) and odd (bottom curves) with respect to the plane containing the three carbon atoms. Dashed lines indicate propene and solid lines cyclopropane.

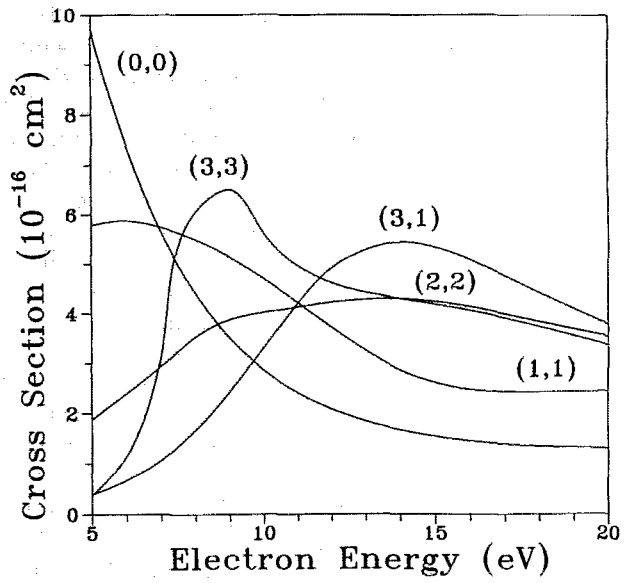

FIG. 3. Major partial-wave (l_{out}, $\pm m_{out}$) contributions to the integral elastic cross section of cyclopropane.

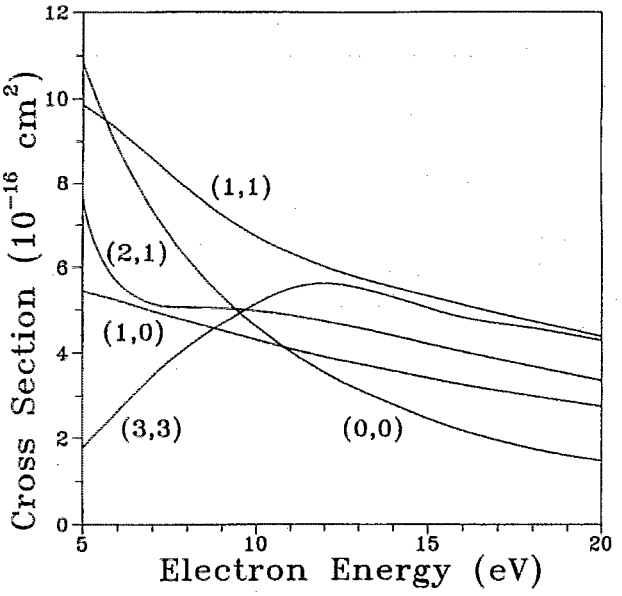

FIG. 4. As in Fig. 3, for propene.

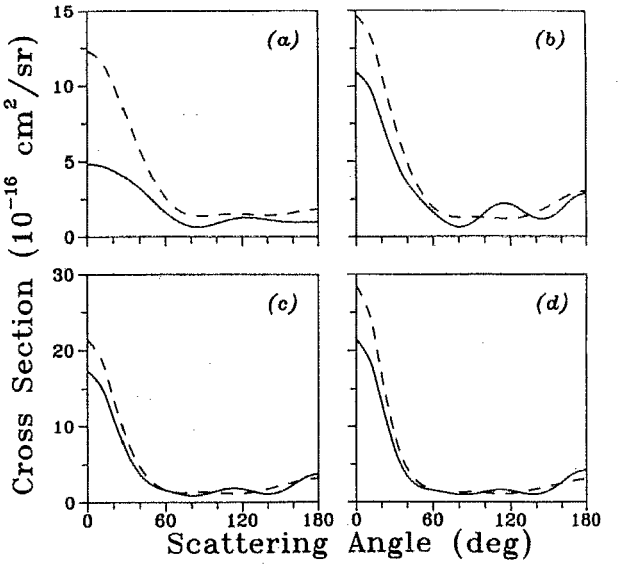

FIG. 6. Differential elastic cross sections for cyclopropane (solid curves) and propene (dashed curves) at (a) 5 eV, (b) 8 eV, (c) 10 eV, and (d) 12 eV.

IV. DISCUSSION

Several interesting features of the results presented above are worth examining. First of all, there is the shift of the broad maximum in the integral elastic cross section for both molecules to higher energies than in the small alkanes.[6–8,10] For cyclopropane, there is also a peak near 8.5 eV whose origin is not immediately clear. The isomeric difference in integral cross section was found to be due to enhanced forward scattering in propene, and the differential cross section of cyclopropane was seen to exhibit low-energy structure not found in propene. In this section we suggest possible explanations for these observations.

Forward scattering should be enhanced in propene relative to cyclopropane by the presence of a dipole moment, leading also to a larger integral cross section. Most of the difference between the two molecules is indeed in the near-forward scattering, as was seen in Figs. 6 and 7; however, not all of this difference can be attributed to the dipole scattering (see Sec. II). The less compact structure of propene probably plays a role also, as suggested in Ref. 8. The fact that the additional scattering by propene is concentrated at small angles of course explains our earlier observation that the momentum-transfer cross sections are nearly the same for the

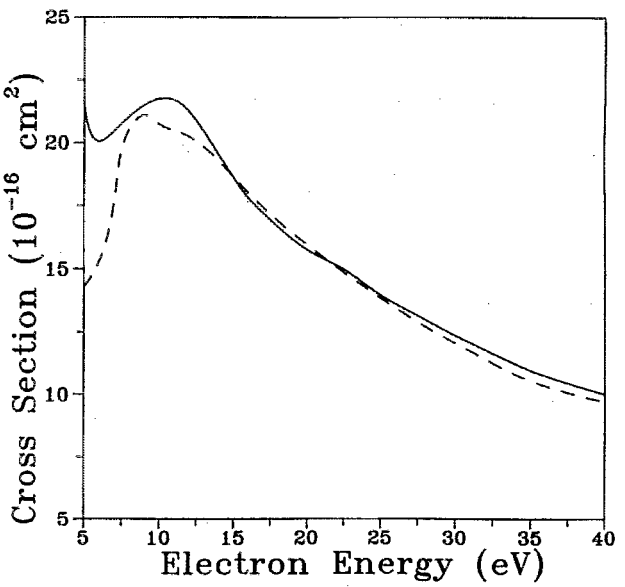

FIG. 5. Momentum-transfer cross sections for cyclopropane (solid curve) and propene (dashed curve).

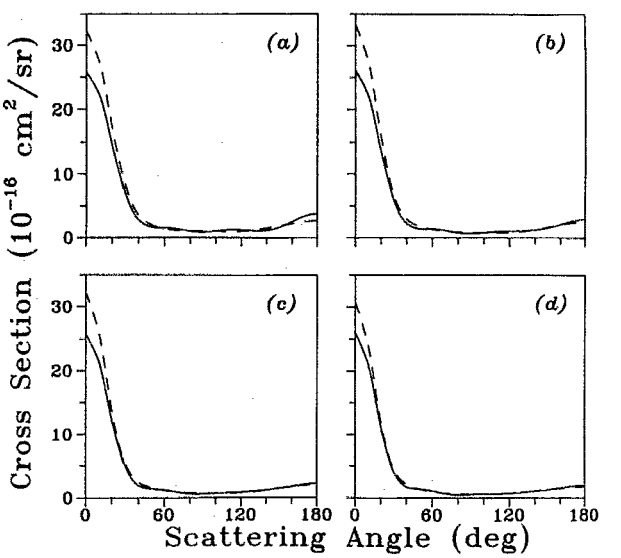

FIG. 7. As in Fig. 6, at (a) 16 eV, (b) 20 eV, (c) 25 eV, and (d) 30 eV.

two molecules (Fig. 2): the $(1-\cos\theta)$ factor in the momentum-transfer cross section gives very little weight to near-forward scattering.

The peak at 8.5 eV in cyclopropane is attributable to an unusual type of shape resonance in A_2' symmetry of D_{3h}, i.e., symmetric with respect to the CCC (σ_h) plane but antisymmetric in each of the three σ_v planes. Several pieces of evidence support this conclusion. An SCF calculation using a minimal basis set[20] places an A_2' virtual valence orbital at 8.4 eV, in very good agreement with the location of the calculated resonance. The resonance was found to occur in the component of the cross section even with respect to the CCC plane, as expected for A_2'; moreover, since this orbital possesses three nodal planes, the first partial wave to which it can contribute is $l=3$, $m=\pm 3$, which was seen above to be the resonant symmetry.

The A_2' virtual orbital is an out-of-phase combination of carbon $2p$ orbitals lying at 60° to the C–C bond direction. In the usual nomenclature, this resonance could be viewed as having nominally 25% C–C σ^* and 75% π^* character. In analogy with the classification of hybridized carbon bonds as sp, sp^2, etc., the resonance might thus be termed $(\sigma\pi^3)^*$. If we take this simple picture to an extreme and compute a zeroth-order resonance energy using a two-component wave function $(\sqrt{3}/2)\pi^* + \frac{1}{2}\sigma^*$ together with π^* and σ^* energies of 4 eV (the static-exchange value for propene) and 13.6 eV (from a minimal-basis calculation on ethane), we predict 6.4 eV for the "$(\sigma\pi^3)^*$" energy, which, considering the crudeness of the model, agrees fairly well with the actual position.

No evidence of such a resonance was found in the measured total cross sections.[7,8] This is not surprising, since there is already a large nonresonant background at 6 eV, approximately where it should be observed. As seen above (Fig. 1), the background also masks the resonance in the calculated integral elastic cross section. However, the effect of the resonance may well be observable in the differential cross section. Indeed, the oscillatory component we observed at low energies (Fig. 6) in cyclopropane, but not in propene, is almost certainly due to this resonance. It may also be possible to observe the resonance in the excitation cross sections for vibrational modes in which the C–C distance changes. Measurements of both kinds would be very interesting.

The shift of the broad maximum in the integral elastic cross section to higher energies in comparison to the alkane series can be explained on the basis of nature of the C–H bonding in these two compounds, if we assume that the maximum is due, at least in part, to short-lived C–H σ^* resonances.[10,21] Three of the six hydrogens in propene are involved in sp^2 bonds. In cyclopropane, the large ring strain leads to orbital hybridization which departs significantly from that of alkanes, and all six hydrogens are bonded to what are approximately sp^2 orbitals.[22] The C–H σ^* orbitals conjugate to these stronger, more localized bonds are expected, in a two-level model, to lie higher in energy than the σ^* orbitals of the alkanes, accounting for the shift in position of the broad maximum. Although this explanation is somewhat speculative, and differences in the inelastic components may also influence the total cross section, a similar shift is seen in the cross sections of ethene[7,10,23] and 1-butene.[7]

In summary, we have reported theoretical elastic scattering cross sections for the C_3H_6 isomers propene and cyclopropane. Enhanced forward scattering in propene, due in part to a weak dipole moment, was found to account for its larger integral cross section, while having little effect on the momentum-transfer cross section. A shape resonance in cyclopropane, related to the alkene π^* resonance but modified by an admixture of σ^* character, was found by analyzing the integral cross section into partial-wave components, although the integral cross section itself shows only a very broad maximum.

The present work, though rather modest in comparison to the capabilities of the DELTA machine, provides a partial demonstration of the power of distributed-memory parallel computing as applied to electron-molecule scattering problems. In the future we hope to extend these calculations by incorporating target polarization and electronic excitation, and to examine as well the cyclobutane cross section, where a shape resonance analogous to that of cyclopropane might be expected to occur.

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